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Sampling and Analysis of Butadiene at a Synthetic Rubber Plant

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16. ABSTRACT

Butadiene emission samples were collected from the process vent stream of a plant manufacturing synthetic rubber from styrene and butadiene. Samples were collected by modification of the evacuated container sampling procedure, outlined in Section 7.1.1 of EPA Method 18. On-site analysis of samples was performed using a gas chromatograph equipped with a flame ionization detector. The precision of butadiene concentrations determined from simultaneous samples collected at a nominal sampling rate of 0.050 L/min, rather than at the recommended sampling rate of 0.5 L/min, was determined. In addition, simultaneous samples were collected at both 0.20 L/min and 0.050 L/min and analyzed to determine if the mean values or precisions of the measured concentrations were influenced by the sampling rate. Acceptable precision was observed upon analysis of emission samples collected at both sampling rates, and the mean values and precisions of butadiene levels determined were statistically equal for simultaneous samples collected using the two sampling rates.

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SAMPLING AND ANALYSIS OF BUTADIENE AT A SYNTHETIC RUBBER PLANT

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

1,3-Butadiene is being evaluated for future emissions regulations because this and other alkenes are quite reactive under atmospheric conditions and exist as "central constituents in urban smog chemistry". Acceptable measurement methodology is critical for proper assessment of the impact on the environment of these emissions from stationary sources. Development and validation of measurement methods are key components for producing an acceptable method. This study was undertaken to perform development and validation work on a method for the quantification of butadiene emissions from stationary sources.

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ABSTRACT

Butadiene has been listed as a hazardous air pollutant by the United States Environmental Protection Agency (EPA). This document details a field study commissioned by the EPA's Environmental Monitoring Systems Laboratory, Quality Assurance Division, Research Triangle Park, North Carolina, that validates a method for the sampling and analysis of butadiene emissions from a stationary source. Butadiene emission samples were collected from the process vent stream of a plant manufacturing synthetic rubber from styrene and butadiene. Samples were collected by modification of the evacuated container sampling procedure, outlined in Section 7.1.1 of EPA Method 18. On-site analysis of samples was performed using a gas chromatograph equipped with a flame ionization detector. The precision of butadiene concentrations determined from simultaneous samples collected at a nominal sampling rate of 0.050 L/min, rather than at the recommended sampling rate of 0.5 L/min, was determined. In addition, simultaneous samples were collected at both 0.20 L/min and 0.050 L/min and analyzed to determine if the mean values or precisions of the measured concentrations were influenced by the sampling rate. Acceptable precision was observed upon analysis of emission samples collected at both sampling rates, and the mean values and precisions of butadiene levels determined were statistically equal for simultaneous samples collected using the two sampling rates.

This report was submitted in fulfillment of EPA Contract No. 68-02-4442 by Entropy Environmentalists, Inc. under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from February 1988 to June 1988 and work was completed as of September 1988.

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ABBREVIATIONS

butadiene	used synonymously with 1,3-butadiene
cm	centimeter(s)
cm H_2O	pressure equivalent to that exerted by a water column of the indicated height
EMSL, QAD	Environmental Monitoring Systems Laboratory, Quality Assurance Division of the United States Environmental Protection Agency
Entropy	used synonymously with Entropy Environmentalists, Inc.
EPA	United States Environmental Protection Agency
FID	flame ionization detector
GC	gas chromatograph
GC/ECD	gas chromatograph equipped with an electron capture detector
GC/FID	gas chromatograph equipped with a flame ionization detector
hr	hour(s)
kPa	kilopascals
L	liter(s)
L/min	liter(s) per minute
m	meter(s)
mL	milliliter(s)
mL/min	milliliter(s) per minute
ppm_v	parts per million by volume
PVC	polyvinyl chloride
quad-train	apparatus for simultaneous collection of quadruplicate samples
ul	microliter(s)

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SECTION 1

INTRODUCTION

1,3-Butadiene (hereafter butadiene) is being evaluated for future emission regulations by the U. S. Environmental Protection Agency. This and other alkenes are quite reactive under atmospheric conditions and exist as "central constituents in urban smog chemistry."[1] In addition, butadiene has been listed as a hazardous air pollutant, in consideration of the serious health effects, including, cancer, resulting from exposure to the substance.[2] A wide variety of natural and manmade combustion processes produce the gas, but the compound is made commercially from dehydrogenation of butene or butane/butene mixtures.[3] Butadiene is widely employed as a polymer building block, particularly in the production of synthetic rubbers as a copolymer with styrene.[4] An analytical method for the measurement of butadiene emissions from polymer-producing processes, as well as from petroleum cracking operations, where the material is produced, is needed.

Entropy Environmentalists, Inc. (hereafter Entropy) performed a field evaluation of a sampling and analysis method for butadiene emissions. This method utilized Tedlar bag sampling and sample analysis using a gas chromatograph equipped with a flame ionization detector. For emission measurements using Tedlar bag sampling, EPA Method 18[5] recommends a sampling rate of 0.5 L/min; thus, an integrated sample collected over 1 hr requires a bag size of approximately 50 L or more for stack emissions sampling. The resulting sample volume is approximately 30 L, while the analysis of the bag contents using a GC requires a far smaller volume, certainly less than a liter, for a number of replicate analyses. The sampling method employed in this evaluation utilized lower sampling rates and, thus, the gas volumes collected were greatly reduced. Acurex Corporation, as part of a previous assignment for EPA's Environmental Monitoring Systems Laboratory, Quality Assurance Division, developed this prototype gas sampling system, which utilizes a reduced sampling rate of 0.050 L/min and which allows the use of smaller, 5 L bags to contain the 3 L sample

collected during 1 hr. Acurex evaluated application of this methodology to the sampling and analysis of butadiene in a laboratory study.[6]

This report describes the field study commissioned by EMSL, QAD, Research Triangle Park, North Carolina, that validates sampling and analysis of butadiene emissions from a synthetic rubber plant using EPA Method 18, modified as described above.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Four principal conclusions were drawn from the data collected and from the observations made during the field test. The sampling and analytical protocol was validated for use at synthetic rubber plants, including the use of the lowered sampling rate utilized for collection of emission samples in small Tedlar bags. The physical and chemical composition of the process effluent encountered in this investigation leads to two important conclusions/recommendations concerning sampling methodology and to two important conclusions/recommendations concerning sample analysis.

USE OF LOWERED SAMPLING RATE

Butadiene levels determined in samples collected in 5 L Tedlar bags at an approximate flow rate of 0.050 L/min and in samples collected in larger, 20 L bags at an approximate flow rate of 0.20 L/min were compared using a Student's t test and the null hypothesis (using the t test). Determinations using the two sampling protocols were found to be equivalent at the 95% confidence level. At the 95% confidence level, there is no bias in the results between the two different sampling rates.

Because a sampling rate of 0.5 L/min, the sampling rate recommended by EPA Method 18, results in a sample volume of approximately 30 L during a 1 hr sampling period, a bag size of approximately 50 L would be required to contain a single emission. Because of the large number of samples required to be taken for this study. Less than a liter of this inconveniently large sample is required for a number of replicate analyses using a GC/FID. Because the two differing sampling rates utilized for collection of bag samples during this study did not statistically affect the values or precisions of the determinations made, the sampling rate of 0.050 L/min, which yields a more convenient sample size than the sampling rate recommended in EPA Method 18, is acceptable for collection of bag samples. Because of the large number of samples that had

to be collected during the comparison of the large and small flowrate the high level flowrate was actually 0.2 L/min and not 0.5 L/min.

ELIMINATION OF ENTRAINED LIQUID FROM THE PROCESS VENT STREAM

The presence of aspirated organic droplets in the process vent stream made the precise quantitation of gaseous butadiene levels very difficult. The precision among quad-train samples was effectively improved by the use of filtering media designed to eliminate such liquid while passing butadiene gas. During this investigation, a glass, liquid knockout chamber, incorporating a fritted glass filter, was used to remove most of the liquid passing to the sample manifold. Because visible amounts of liquid were carried past this filter, the sample stream was next directed through a small tube containing the porous polymer XAD-2, which shows little affinity for butadiene; gas was then passed to a stainless steel manifold. When these measures were instituted, the average coefficient of variation observed using the small bags was approximately 7%.

As noted above, the elimination of entrained liquid in the process vent stream was necessary to improve the precision observed upon analysis of simultaneous samples collected during this study. Therefore, the elimination of similar liquids from other process effluents is highly recommended for collection of bag samples. Further investigation of filtering media designed to accomplish this while passing the sample component of interest is recommended.

PRESENCE OF HYDROCARBON INTERFERANTS

The presence of several butane/butene isomers in the sample stream necessitated the use of a chromatography column capable of separating butadiene from these potential interferants. A 2 m x 1/8" stainless steel column containing 0.19% picric acid on 80/100 mesh Carbopack C was utilized during this investigation. This column, or another column similarly able to resolve butadiene from these potentially interfering hydrocarbons, is highly recommended.

USE OF A TWO COLUMN BACKFLUSH-TO-VENT CONFIGURATION

Sample analysis involved a chromatographic system utilizing a backflush-to-vent configuration designed to prevent high boiling sample components from reaching the picric acid column, the second column in a serial two column

arrangement. The first column, a 10' x 1/8" stainless steel column containing 20% SP-2100/0.1% Carbowax 1500 on 100/120 mesh Supelcoport, effected the separation of butadiene and other permanent gases from higher boiling sample components within approximately three minutes. The separation of butadiene from butane and butene isomers was completed on the picric acid column, allowing sample analysis to be completed in under 12 minutes. This system allowed accurate quantitation of butadiene in the observed sample matrix to be carried out far more rapidly than is possible with a conventional single column system; use of a similar system is recommended to expedite the analysis of butadiene samples whenever significant quantities of higher boiling organics are present.

SECTION 3

SUMMARY OF EXPERIMENTAL APPROACH AND RESULTS

The experimental approach for validating the application of Method 18 to the measurement of butadiene emissions using a modified sampling rate necessarily considered all aspects of the method. Thus, the format of the method itself was adopted in the procedural summary outlined below. Some aspects of the study are further detailed in the sections that follow this summary.

The experimental approach was designed to provide the data and documentation necessary to validate modification of the sampling rate specified by EPA Method 18 while evaluating application of the method to the sampling and analysis of butadiene.

APPLICABILITY AND PRINCIPLE

The principles of sampling and analysis followed the general procedures described in EPA Method 18, with the exception that emission samples were collected at flow rates of 0.050 L/min and 0.20 L/min, rather than 0.5 L/min.

RANGE AND SENSITIVITY

The range and sensitivity were determined for the Tedlar bag sampling technique prior to conducting the field test. An estimation of the limit of detection and quantifiable limit was carried out as described by Joseph Knoll of EMSL, QAD in the Journal of Chromatographic Science.[7] Using a sample size of 1 mL, these values were determined to be 0.43 ppm_v and 2.0 ppm_v respectively.

The upper limit of detection, where the GC column becomes saturated and/or the detector response becomes non-linear, was also estimated. The peak shapes observed for prepared samples that contained butadiene at levels of approximately one percent indicated that the column was saturated. The retention time observed for these prepared samples was also significantly shortened. The shift in retention time was potentially great enough to prevent the complete separation of butadiene from other components observed in samples collected during the field tests. Emission levels quantified in the field test

ranged from about 10 to 3500 ppm_v, always below the estimated upper limit of the chromatographic system.

PRECISION AND ACCURACY

Some specific on-site modifications of the sampling procedures were made to improve the precision and accuracy of the data obtained during the first field test. These sampling modifications were used during the second field test, and a chromatographic system that rapidly and more accurately quantified butadiene levels was developed in the time period between the tests. For these reasons, a full discussion of only the results from the second field test is included in this report.

Precision of Sampling and Analysis

The precision of the sampling and analysis techniques was determined using quad-trains. For the field tests, gases were withdrawn from a duct carrying process emissions in route to an open flare. All four bags were analyzed on-site, as was an audit sample. The results from analysis of the four bags were averaged and a standard deviation, variance, and 95% confidence interval for each sampling run were calculated. Much of this information is summarized in Table 1.

Dickson's test[8] revealed that the values obtained from one sample each in sampling runs 52 and 56 could be discarded as statistical outliers at a confidence level of 95%. Two estimates for measures of the precision of the method are given, one in which the outliers are included and one in which they are not.

Small bag samples--

For butadiene levels measured using samples collected in the small Tedlar bags, linear regression of the standard deviation on the populations' means indicated that the standard deviations determined for the twelve individual sampling runs were not level dependent over the observed range of 10 to 3500 ppm_v. A pooled standard deviation for use of the small bag samples is not reported because Bartlett's test for homogeneity of variances showed that calculation of such a pooled value is inappropriate. The absence of a level dependence and the inappropriateness of calculating a pooled standard deviation

TABLE 1. SUMMARY OF ANALYTICAL RESULTS AND PRECISION OF DATA

Date	Run ID	Mean*	Std. Dev.	Coef. of Var.(%)	Variance
4/28	51	322	7.4	2.3	55
4/28	52@	24	5.7	24	32
4/28	53	30	3.7	7.8	61
4/28	L54**	444	47	11	2200
4/28	54	459	39	8.5	1500
4/28	55	171	17	9.8	279
4/28	56@	546	150	27	21000
4/29	61	426	76	18	5700
4/29	62	29	3.0	10	9.0
4/29	63	114	11	10	120
4/30	71	149	6.6	4.5	44
4/30	L72	14	0.6	5	0.3
4/30	72	13	0.4	3	0.2
4/30	73	3480	40	1.2	1800

* Butadiene concentrations in ppm_v.

** One bag sample collected during this run was found to leak; the results from analysis of this bag are not included in any statistical evaluation of the data.

@ The results summarized below are obtained for sample runs 52 and 56 when statistical outliers are excluded.

Date	Run ID	Mean*	Std. Dev.	Coef. of Var.(%)	Variance
4/28	52	27	1.4	5.1	2
4/28	56	473	15	3.1	217

held true whether calculation of means, standard deviations, and variances for the sample runs did or did not include the two individual samples shown to be statistical outliers.

The average coefficient of variation observed for all the small bag samples was approximately 11%, but dropped to 6.9% when the two statistical outliers were eliminated from their respective sample sets and the means and standard deviations of those samples recalculated accordingly.

Large bag samples--

Because only two sample runs at observed butadiene levels of 14 and 444 ppm_v utilized the large Tedlar bags, no attempt was made to determine if the observed standard deviations were level dependent or if calculation of a pooled standard deviation was appropriate. The average coefficient of variation observed for these two runs was approximately 8%; the analysis of one large bag sample collected as part of these runs was discarded because the bag did not pass a post-analysis leak check.

Comparison of Results Obtained Using Both Bag Sizes

During one dual quad-train sampling run, the butadiene level determined using samples collected in the small Tedlar bags at an approximate flow rate of 0.050 L/min was 459 ppm_v and the standard deviation observed among the four replicates was 39 ppm_v. The level determined using the large bag samples collected at a flow rate of about 0.20 L/min was 444 ppm_v and the observed standard deviation was 47 ppm_v. For the other dual quad-train run, the level measured using the small bags was 13 ppm_v, with a standard deviation of 0.6 ppm_v, while the respective data collected using the large bags were 13 ppm_v and 0.4 ppm_v. A variance-ratio test, or F-test, showed that standard deviations obtained using the different bag sizes and flow rates were not significantly different at the 95% confidence level for either of the two sampling runs. This fact, and the similarity of the average coefficients of variation calculated after analysis of samples collected using both sampling rates, suggests that the precisions for the two sampling protocols are invariant with respect to sampling rate. Likewise, when the means of butadiene levels determined using the small and large Tedlar bags were compared for the two sampling runs using a Student's t test and the null hypothesis (using the t test), they were found to be equivalent at the 95% confidence level.

Within-Laboratory Precision

For individual bag samples, successive duplicate analyses were always well within 5% of their mean value as required by the EPA Method 18. In fact, the duplicate analyses often differed from the mean by less than 1%.

One small bag sample from nine of the first ten sampling runs was returned to the base laboratory for reanalysis by Entropy. All bags collected during the final two sampling runs, except one sample from the twelfth run that leaked, were also retained. A full complement of four large and four small bags was available as the eleventh sampling run involved sample collection using the dual quad-train setup. These samples were analyzed within one week of completion of the field test. The average coefficient of variation for the field and laboratory analyses of samples collected in small bags was 9.5%; the average coefficient of variation was 13% when the precisions of both small and large bags are included. The reanalysis results are given in Table 2.

Between-Laboratory Precision

Following reanalysis at Entropy's base laboratory, selected bag samples were made available to EMSL, QAD personnel for independent verification of butadiene concentrations measured. The precisions of the post-field test analyses performed by Entropy and EMSL, QAD were calculated. The average coefficient of variation for the analyses of these retained bag samples at the two laboratories was 4.9%. These results are collected in Table 3.

Audit Results

The accuracy of the butadiene determinations was examined by the on-site analysis of a blind audit sample provided by Research Triangle Institute, Research Triangle Park, North Carolina under the EPA's performance audit program, which utilizes cylinder gases containing volatile organics in the ppm_v range. The audit cylinders available were known to contain butadiene in the 5-60 ppm_v range. Field and laboratory analyses of the cylinder provided a quality assurance check of the three-point calibration curves covering the approximate range 10 to 2000 ppm_v.

Several analyses of the audit cylinder were conducted while analyzing samples collected during the field test. The average value obtained for the concentration of the audit cylinder was approximately 6% below the certified concentration.

TABLE 2. COMPARISON OF FIELD AND LABORATORY ANALYSES

Sample ID	Field Conc. (ppm_v)	Lab Conc. (ppm_v)	Avg. Conc. (ppm_v)	Coef. of Variation	Age (Days)
51-A	331	336	334	1.1%	7
52-A	28	26	27	5.2%	8
53-A	33	37	35	8.1%	8
54-C	401	386	394	2.7%	7
55-D	188	163	176	10%	7
56-A	486	424	455	9.6%	7
61-C	419	242	331	38%	6
62	NO SAMPLE FROM THIS RUN WAS RETAINED FOR LAB ANALYSIS				
63-D	122	87	105	24%	7
71-D	154	144	149	4.7%	6
72-A	12.5	14.5	13.5	10%	6
72-B	13.1	14.5	13.8	7.2%	6
72-C	13.3	13.7	13.5	2.1%	6
72-D	12.6	14.2	13.4	8.4%	6
73-A	3480	3300	3390	3.8%	5
73-C	3530	2760	3140	17%	5
73-D	3480	2700	3090	18%	5
L72-A	13.1	16.3	14.7	15%	6
L72-B	14.3	22.3	18.3	31%	6
L72-C	14.4	20.1	17.3	23%	6
L72-D	13.5	17.0	15.3	16%	6

TABLE 3. COMPARISON OF BAG SAMPLE ANALYSES PERFORMED BY ENTROPY AND EMSL, QAD

Sample ID	Entropy Analysis (ppm_v)	EMSL, QAD Analysis (ppm_v)	Average Result (ppm_v)	Coefficient of Variation
72-A	14.5	13.5	14.0	5.1%
72-B	14.5	14.5	14.0	0.0%
72-C	13.7	14.0	13.8	1.5%
72-D	14.2	13.5	13.8	3.6%
73-A	3300	3300	3300	0.0%
73-C	2760	3000	2880	5.9%
73-D	2700	2800	2750	2.6%
L72-A	16.3	14.5	15.4	8.3%
L72-B	22.3	18.5	20.4	13%
L72-C	20.1	16.5	18.3	14%
L72-D	17.0	17.0	17.0	0.0%

INTERFERENCES

Several other organic components in addition to butadiene were present in samples collected from the plant's process vent. Reanalysis of samples retained from the first field test on a megabore capillary column by the EPA Task Officer revealed the presence of several butane/butene isomers. Unfortunately, the retention times of some of these coincided with the retention time of butadiene on the column used for the first field test. This column, a 10' x 1/8" stainless steel column containing 20% SP-2100/0.1% Carbowax 1500 on 100/200 mesh Supelcoport, did not exhibit sufficient resolving power for accurate quantitation of the diene when used alone. For the second field test, sample analysis involved a chromatographic system utilizing both the 20% SP-2100/0.1% Carbowax 1500 column and a second column containing 0.19% picric acid on 80/100 mesh Carbopack C.

PRESURVEY

Pretest samples were developed to determine any need for modification of the sampling procedures. After discussions with plant officials concerning the

chemicals present in the process vent stream, gaseous mixtures were prepared in Tedlar bags to examine the chromatographic separation for the expected process exhaust gases. In particular, separation of the analyte from styrene, known to be present in the process output, was examined on two columns. These were: 1) 60/80 Carbopack B/1% SP-1000 and 2) 20% SP-2100/0.1% Carbowax 1500 on 100/120 Supelcoport. The former column was used in a laboratory study during development of test methods for GC analysis of butadiene, and in a field test that quantified butadiene in samples collected from a hydrocarbon synthesis plant, performed previously by Acurex Corporation.[6] The latter column was chosen for use during the first field test of this investigation because of the rapidity of successive analyses it allowed, a factor critical for completing analysis of all samples on-site.

Following the first field test, it was discovered that determinations of butadiene in samples collected during this field test exhibited a bias. Because the peak which eluted from the 20% SP-2100/0.1% Carbowax 1500 column at a retention time corresponding to butadiene was a composite, the on-site analyses of samples during the first test exhibited a high bias. These results, therefore, are included only as part of Appendix B and are not discussed in the main body of this report. As discussed below, the analysis of field samples was modified to give more accurate quantitation of butadiene during a second field test.

ANALYSIS DEVELOPMENT

Two major concerns with all organic sampling and analytical procedures are 1) rapidity of sample analyses and 2) sample stability. To address the first point, minimization of time required for the total elution of individually injected samples was considered in selection of GC conditions for analysis of field samples. Sample stability was assessed by reanalysis of field samples after "aging".

Development of Chromatographic Separation

For the final field test, sample analysis involved a chromatographic system utilizing 1) two packed GC columns connected in series to give adequate separation of closely related hydrocarbons from butadiene, and 2) a backflush-to-vent configuration designed to prevent high boiling sample components from reaching the second column. The first column, a 10' x 1/8" stainless steel

column containing 20% SP-2100/0.1% Carbowax 1500 on 100/120 mesh Supelcoport, effected the separation of butadiene and other permanent gases from the higher boiling components, among them styrene, within approximately three minutes. Within that time these gases had passed into the second column, a 2 m x 1/8" stainless steel column containing 0.19% picric acid on 80/100 mesh Carbopack C. A pneumatic valve was activated manually at this point to direct a separate carrier flow through the second column allowing for the separation of butadiene from other permanent gases present, while the original carrier flow was simultaneously reversed through the first column to backflush higher boiling sample components to a vent. The separation was performed isothermally at 60°C, and both carrier flows were approximately 20 mL/min in the forward direction. Utilizing this system, duplicate analyses of bag samples could be completed within 20 minutes, much faster than is possible for accurate quantitation of butadiene in this sample matrix when a single column is utilized for the separation and backflushing is not employed.

Examination of Sample Stability

To assess the stability of the bagged samples, reanalysis of one sample from 11 of the 12 field test sampling runs was undertaken during the week following the field test. In addition, several of the samples collected the last day of the field test were reanalyzed, including all samples from the final run of small bags and all the large and small bags collected during the eleventh sample run. Table 2 shows the results obtained upon reanalysis of bag samples returned to Entropy's laboratory. Because the reanalysis results were in overall agreement with the results obtained during the original on-site analyses, the two sets of measurements were used to estimate a within-laboratory precision for the method as discussed above.

FINAL SAMPLING AND ANALYSIS

During the field test, samples were collected in quadruplicate in the 5 L Tedlar bags. In addition, during two sampling runs, samples were collected using dual quad-trains. One train utilized 5 L bags and the other train utilized 20 L bags. All quad-trains drew gases from a common manifold. Twelve sample runs were conducted during the test.

Tedlar Sampling Bags

Double seamed Tedlar bags were fabricated as described previously.[9] The contents of each was accessed via a bulkhead female quick-connect fixed in the lid of each PVC bag sampler in the case of the small bags; an analogous design was used for the large bags contained in rigid plastic containers. The volume of the small bags was approximately 5 L and that of the large bags was approximately 20 L.

Each bag was leak checked before being used to collect field samples. Bags were inflated to rigidity and allowed to stand overnight or longer. If a bag showed any loss of rigidity, it was discarded. During the field tests, bags to be reused were flushed twice with compressed air to remove previous samples. They were then completely evacuated and allowed to stand for several minutes and examined for the intake of air in order to detect gross leaks. New bags were used for most samples to be retained for post-field test studies. In preparation for the first field test, an effort was made to leak check the bags after loading them into the PVC bag samplers using a procedure developed by the EPA work assignment task officer. The procedure and attempts to utilize it are discussed below.

Sampling Apparatus

A schematic of the sampling apparatus is included as Figure 1. Gas samples were acquired at a duct leading from process vents to an open flare. A probe line constructed of 3/8" Teflon tubing was connected to the duct via connecting fittings provided by plant personnel. The probe was in turn connected to a Teflon-diaphragm sampling pump. The output of this pump was conducted via Teflon tubing to a vertically-mounted glass tube designed to knock out aspirated liquids present in the process stream. This configuration forced gases and liquids entering the tube to flow against gravity. A horizontal opening at the tube's lower end allowed any liquid collecting in the tube to drain continuously under the influence of a portion of the sample flow allowed to vent at this point. The remainder of the sample flow passed through a fritted glass filter before exiting horizontally through another side opening at the glass tube's upper end. To eliminate any fine aerosol passing through

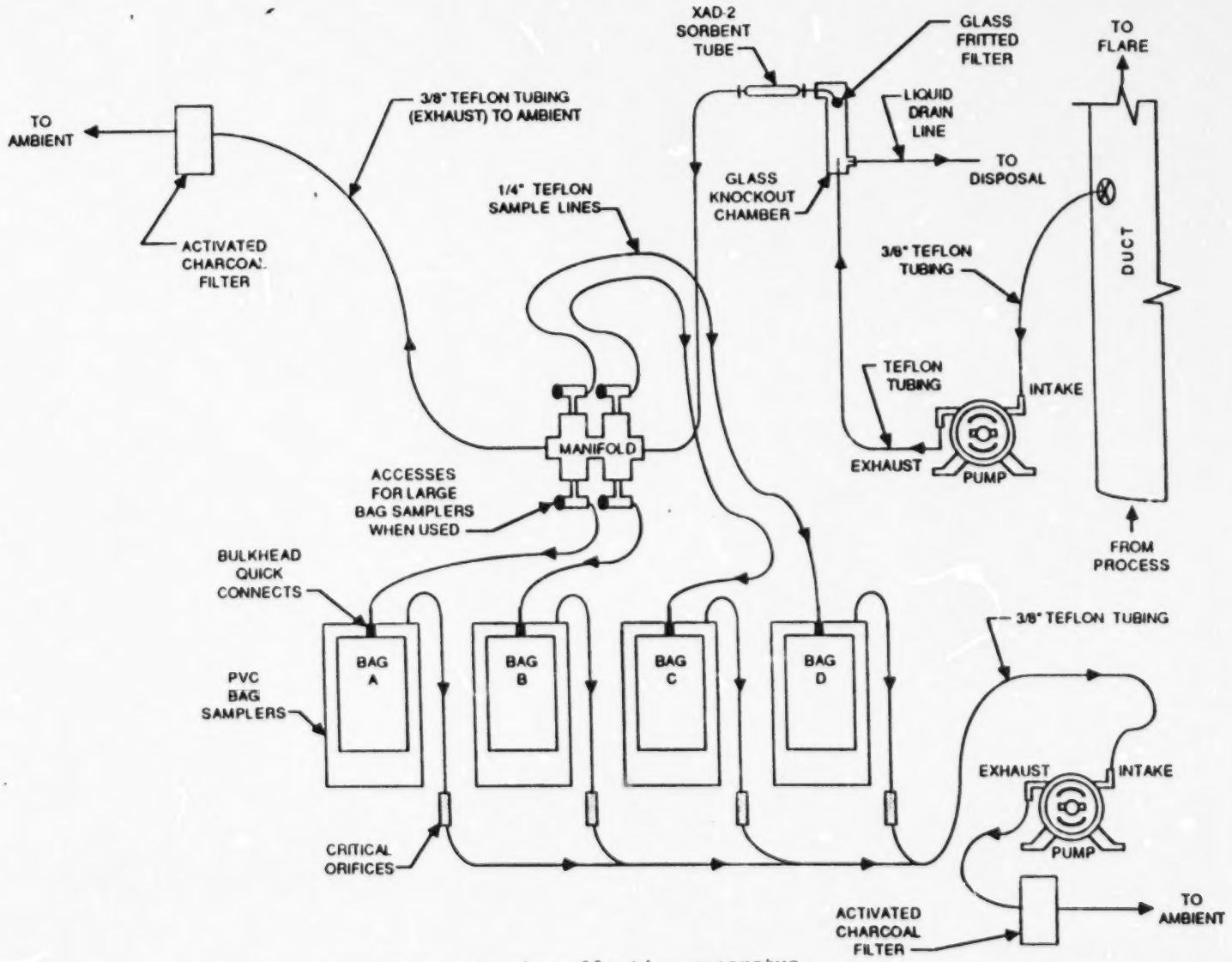

Figure 1. Sample collection apparatus.

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the glass filter, the stream exiting the glass tube was directed through a small tube containing the porous polymer XAD-2, which shows little affinity for butadiene, before passing to a manifold constructed of stainless steel piping. A slight positive pressure, approximately 5 cm H_2O, was created in the manifold by carefully adjusting the flow rate of material exiting the horizontal liquid drain vent in the glass tube containing the fritted glass filter.

Placing the sampling manifold downstream of the pump was necessary to overcome the highly variable duct pressures which rapidly fluctuated from positive to negative pressures, the magnitudes both of which were on the order of several cm H_2O. The exhaust from the manifold was vented to the ambient as the concentrations of butadiene observed were far below the lower explosive limit. Before each sampling run, the manifold was purged with stack gas for several minutes to allow equilibration of the system.

Gas was conducted from the steel manifold to each bag sampler using individual Teflon sample lines, each approximately five feet in length. Each sample line terminated in a self-sealing, male quick-connect. This connect was mated with the female, bulkhead quick-connect, on each bag container lid. The sealed bag samplers were capable of containing the slight positive pressure in the manifold; thus, sample flow into the bags could be controlled by fixing the flow exiting the container. Flow from each container was controlled using a calibrated critical orifice and a sufficiently high pump vacuum behind each orifice so that sonic velocity through each orifice was maintained.

Flow through each of the four orifices in one of two arrays was approximately 0.050 L/min, while flow through those in a second array of four orifices was about 0.20 L/min. The flow rates used to collect samples during each run are presented in Table 4.

PVC Bag Samplers

The PVC bag samplers were provided to Entropy by EPA. The work carried out prior to the field test to improve the performance of the sampling containers during leak check procedures is discussed in Section 4. The design of the containers is included as Figure 2.

TABLE 4. TESTING TIMES AND SAMPLING RATES

Date	Run No.	Sampling Time 24 hr	Sampling Rate cc/min
4/28	51	10:40 - 11:05	200
	52	11:21 - 11:46	200
	53	12:23 - 12:48	200
	54	20:05 - 21:05	50
	L 54	20:05 - 21:05	200
	55	16:55 - 17:25	200
	56	22:23 - 23:23	50
4/29	61	12:07 - 13:07	50
	62	14:26 - 14:56	200
	63	16:28 - 17:28	50
4/30	71	09:23 - 10:23	50
	72	10:50 - 11:50	50
	L 72	10:50 - 11:50	200
	73	14:43 - 15:13	200

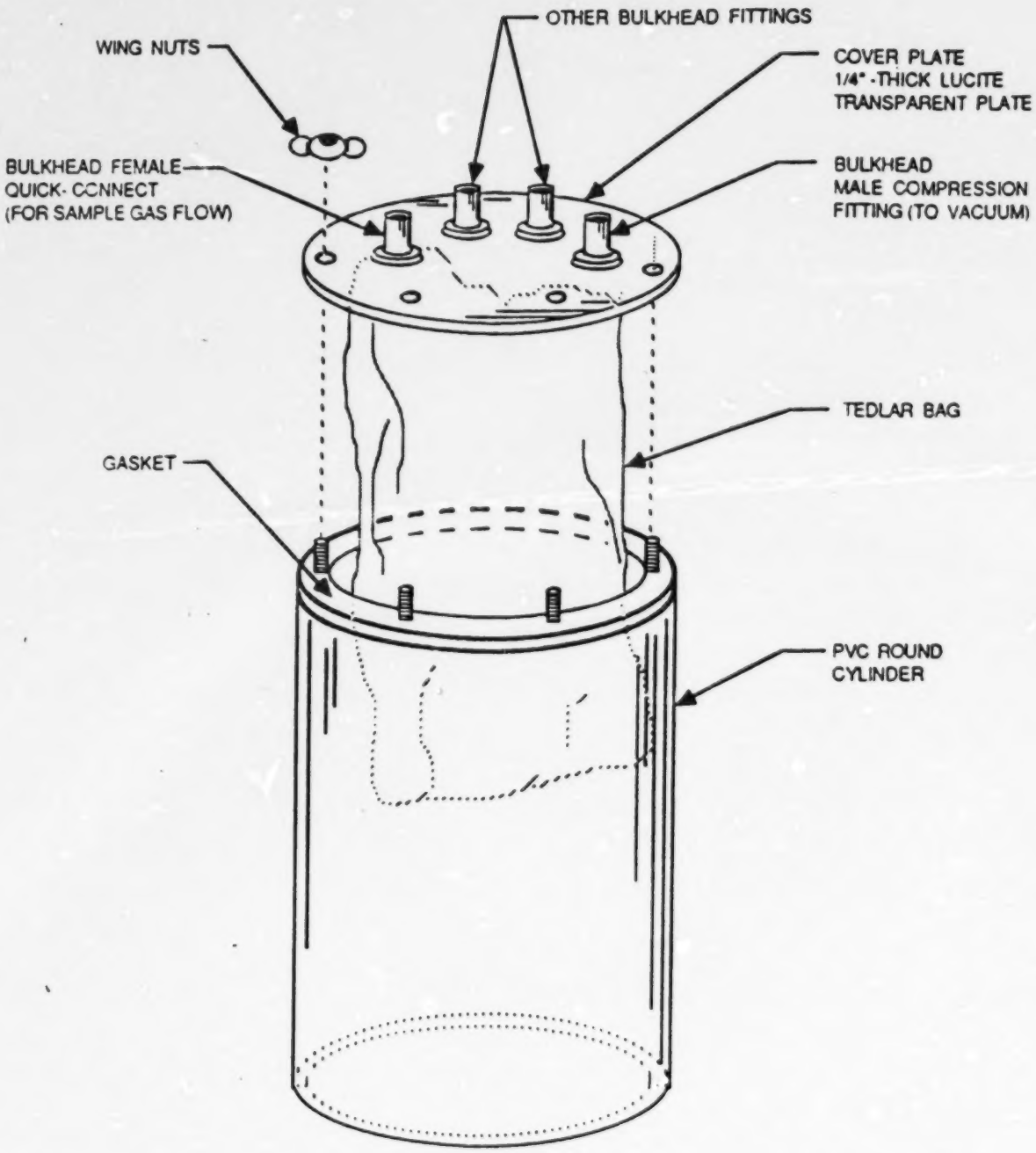

Figure 2. PVC bag sampler.

SECTION 4

QUALITY CONTROL

During each stage of the investigation every effort was made to guarantee the integrity of the data collected. Some of the important precautions observed are outlined below.

CYLINDER STANDARDS

Analyzed cylinders containing approximately 10, 150, and 2000 ppm_v of gaseous butadiene in nitrogen were purchased from a supplier of high purity gases. The cylinders were analyzed after final blending by the supplier, who certified the butadiene concentrations to $\pm$ 2%. No other standards were necessary for completion of the field test or lab work.

CALIBRATION AND AUDIT PROCEDURES

Calibration standards were injected into the gas chromatograph until two successive injections disagreed by no more than 5%, as specified in EPA Method 18. Often duplicate injections of standards, and those of most samples, differed from their mean by less than 1%.

Instrument response was obtained from a least squares fit of the calibration data. An audit of these results was conducted daily by assaying the concentration of a blind audit sample provided under the EPA's performance audit program. The audit sample contained butadiene diluted with nitrogen gas at a concentration in the ppm_v range.

MODIFIED LEAK CHECK OF BAGS IN PVC BAG SAMPLERS

Because the modified leak check procedures required a GC equipped with an electron capture detector and this instrumentation was not available at Entropy, development of such procedures was attempted at EMSL, QAD with the aid, and under the direct supervision, of the EPA work assignment task officer.

To check for leaks, liquid 2-bromopropane was introduced into the void space surrounding each bag in a number of the PVC containers. The injection of

2 uL yielded a final concentration of approximately 10 ppm_v of 2-bromopropane vapor in the void space. After about 30 minutes, the contents of each bag were analyzed using a GC/ECD. Detection of 2-bromopropane inside the bag was indicative of a leak. Carbon tetrachloride was used in place of 2-bromopropane during attempts to overcome problems encountered during these leak checks. Because further problems were encountered, only a portion of the bags used for the first field test were checked using these procedures.

RETENTION OF BUTADIENE BY TEDLAR BAGS

Although the retention of butadiene by Tedlar bags was not rigorously evaluated, experiments were conducted to demonstrate that bags containing field samples could be reused after they had been reblanked. Bags were emptied of sample by complete evacuation and flushed twice with compressed air before being filled to half their capacities. After allowing the bags to stand overnight, analysis of the contained gas showed them to be essentially free of butadiene.

SECTION 5

ANALYTICAL INSTRUMENTATION AND OPERATING PARAMETERS

Prior to the field test, efforts were expended to improve the speed and convenience of sample analysis. These efforts are described below.

All samples were analyzed using a Hewlett-Packard 5890 GC equipped with an FID. For all analyses, the hydrogen and air flow rates to the FID were fixed by supplying these gases at constant regulator pressures to the instrument's internal metering orifices. The approximate pressures and resulting flow rates were selected by consulting literature provided by the manufacturer. No attempt was made to optimize the detector response by further adjustment of the combustion gas flows.

Peak areas were determined using a Spectra Physics 4290 electronic integrator. The detector output to the integrator was maintained at a single attenuation level for all analyses so that no attenuation corrections were applied to areas determined by the integrator. For many samples, the integrator recognized baseline separation between butadiene and the most closely eluting interferant, a peak presumably composed of one or more butene isomers.

Samples were introduced into the GC utilizing a 1.0 ml Teflon sample loop in conjunction with a manually-activated gas sampling valve. Samples were drawn into the loop via a small pump at a nominal flow rate of 100 mL/min.

The column and operating parameters utilized by Acurex Corporation[6] during previous laboratory and field studies were reviewed before the analysis conditions for the current field test were established. The selection of the 20% SP-2100/0.1% Carbowax column, used exclusively for the first field test, and used as part of a two column separation during the second field test, was based on pretest laboratory experiments performed by Entropy. The picric acid column, the second of two columns utilized during the second field test, was chosen for the separation of butadiene from interfering hydrocarbons after discussions with the technical staff of a chromatographic supplier. The chromatographic parameters used for the second field test are summarized in

Table 5, while a more complete discussion of the choice of columns is presented in Section 4.

TABLE 5. GC CONDITIONS FOR ANALYSIS

First Column:	20% SP-2100/0.1% Carbowax on 100/120 mesh Supelcoport (10' x 1/8")
Second Column:	0.19% Picric Acid on 80/100 mesh Carbopak C (2 m x 1/8")
Oven Temperature:	60°C
Sample Valve Temperature:	Same as Oven
Detector Temperature:	300°C
Carrier Flow:	20 mL/min

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5. 40 Code of Federal Regulations 60, App. A, Method 18. July 1, 1987.

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7. Knoll, Joseph E. "Estimation of the Limit of Detection in Chromatography." Journal of Chromatographic Science, 23:422-425, 1985.

8. Quality Assurance Handbook for Air Pollution Measurement Systems, Vol. I - Principles, Appendix F. EPA-600/9-76-005, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1976.

9. Knoll, Joseph E., Mark A. Smith, and M. Rodney Midgett. Evaluation of Emission Test Methods for Halogenated Hydrocarbons, Vol. I - CCl_4, $C_2H_4Cl_2$, C_2Cl_4, and C_2HCl_3. EPA-600/4-79-02, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1979.

APPENDIX A

STANDARD OPERATING PROCEDURES
FOR THE SAMPLING AND ANALYSIS OF BUTADIENE EMISSIONS

1. Applicability, Principle, Interferences, Precision, Bias, and Stability

1.1 Applicability. These procedures are applied in the determination of 1,3-butadiene (hereafter butadiene) present in waste gases emitted from synthetic rubber plants.

1.2 Principle. Gas samples are collected in Tedlar gas sampling bags from a conduit carrying gaseous emissions and analyzed using a gas chromatograph equipped with a flame ionization detector (GC/FID).

1.3 Potential Interferences. Several other organic components in addition to butadiene are generally present in emission samples. The possible presence of several C_4 and unsaturated C_4 hydrocarbons in the emission samples necessitates the use of a chromatography column capable of separating butadiene from these potential interferants.

1.4 Precision. The within-laboratory relative standard deviation observed for the collection and analysis of quadruplicate samples during field validation of this method was approximately 7%.

1.5 Stability. Samples should be analyzed within two weeks of collection.

2. Summary

2.1 Sampling. Emission samples are collected in 5 L Tedlar bags housed in rigid, air-tight PVC containers. Evacuation of the container void space surrounding the bag, at nominal flow rates of 50 mL/min over a 1 hour period, draws a 3 L sample into the bag.

2.2 GC Analysis. Cylinders of dilute gaseous butadiene in nitrogen, commercially available from a supplier of high purity gases, are used as standards in calibration of the GC. The linear calibration curves generated from analysis of these standards are used to determine the concentration of butadiene in collected field samples.

3. Safety

Butadiene has been listed as a hazardous air pollutant in the Federal Register[1] since serious health effects result from exposure to the gas;

therefore, inhalation of butadiene, and of other potentially harmful vapors present in source samples, must be rigorously avoided. The use of electrical equipment for sampling in potentially explosive areas requires additional precautionary measures.

4. Apparatus and Materials

4.1 Sampling Apparatus. The sampling train is shown in Figure A-1, and component parts are discussed below.

4.1.1 Probe. Teflon tubing, 3/8" OD. Attach to a port in the conduit carrying gaseous process emissions via appropriate connecting fittings.

4.1.2 Glass Wool. Borosilicate or quartz. Use a small wad of glass wool at the inlet of the probe to remove particulate matter, if present in the sample stream.

4.1.3 Primary Sampling Pump. Leakfree Teflon-coated diaphragm-type pump, or equivalent. Connect directly to the anterior end of the Teflon probe line.

4.1.4 Liquid Knockout Chamber. Elongated glass vessel with 1/4" openings at either end, incorporating a fritted glass filter at the outlet access and a perpendicular sidearm near the inlet access. The use of the knockout chamber is optional, but is highly recommended to eliminate entrained liquids when they are present in the process stream. Mount the chamber vertically with the outlet end and glass filter facing up. Connect to the outlet of the sampling pump with Teflon tubing so that sample gas and entrained liquid enter the tube at the bottom. The perpendicular sidearm located at the lower end allows any liquid collecting in the tube to be forced out by a portion of the sample flow allowed to vent at this point. The fritted glass filter present at the top of the chamber passes gases subsequently sampled.

4.1.5 Liquid Drain Line. Composed of rubber surgical tubing or other convenient material used in conjunction with the optional liquid knockout chamber. Attach to the sidearm of the knockout chamber. Provide for collection and disposal of liquid exiting at the end of line and for appropriate venting of sample gas (refer to Section 4.1.9).

4.1.6 Flow Control Valves. Connect in-line after the sampling manifold and adjust to maintain slight positive pressures in the sampling apparatus. If the optional liquid knockout chamber is used, include a flow control valve to regulate the flow rate of sample vented via the liquid drain line.

4.1.7 XAD-2 Adsorption Tube. The use of the adsorption tube is optional, but is highly recommended to eliminate entrained liquid when visible quantities are carried past the optional liquid knockout chamber. Place the XAD-2 tube, which will largely pass butadiene, in-line between the knockout chamber and sampling manifold to trap fine liquid droplets.

4.1.8 Sampling Manifold. Stainless steel, with the appropriate fittings necessary for acquisition of simultaneous samples and for connection of a

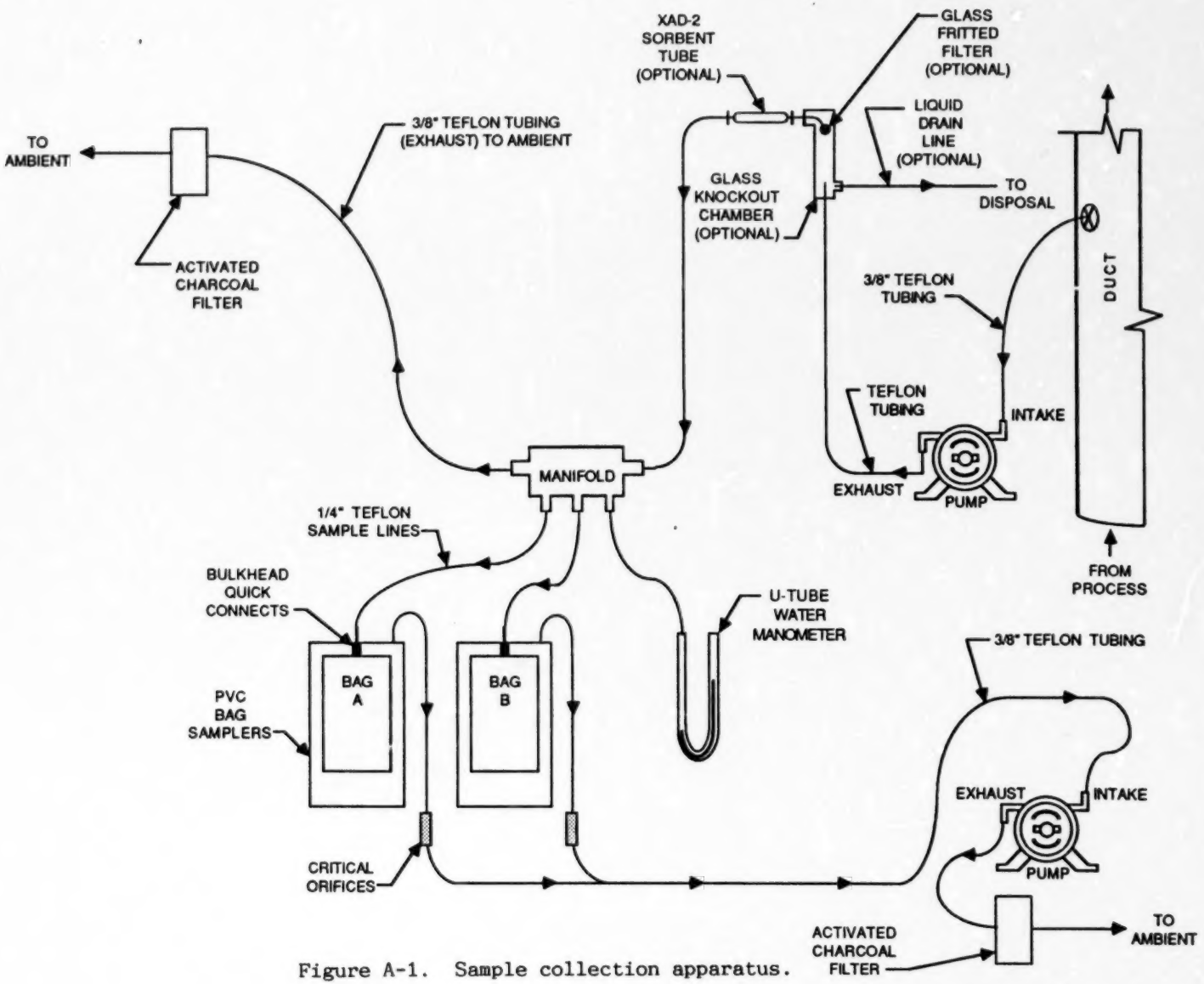

Figure A-1. Sample collection apparatus.

manometer. In general, two or more samples are collected. Flow through all parts of the manifold should be unrestricted and uniform. Connect downstream of the sampling pump using Teflon tubing.

4.1.9 Activated Charcoal Filters. Place behind auxiliary sampling pump to adsorb gas vented in the event of sampling bag rupture. Also place behind sampling manifold to filter gas, if excess is vented to the atmosphere rather than returned to emission conduit.

4.1.10 Manometer. 76 cm. U-tube water manometer, to measure pressure existing in the sampling manifold.

4.1.11 Sample Lines. Teflon tubing, 1/4" OD, to conduct gas from the manifold to the Tedlar gas sampling bags.

4.1.12 Quick-connects. Stainless steel, self-sealing, male quick-connects. Attach to the bag end of each sample line. Mating female, stainless steel, bulkhead quick-connect, affixed in the lid of rigid, evacuable bag containers are adjoined on the underside of each container lid directly to an enclosed Tedlar gas sampling bag.

4.1.13 Rigid, Evacuable Bag Containers. PVC or other suitable rigid material, to house leakfree Tedlar gas sampling bags. The design of one such container is shown in Figure A-2.

4.1.14 Tedlar Gas Sampling Bags. Unused, double-seamed, with nominal capacities of 5 liters.

4.1.15 Auxiliary Sampling Pump. For evacuation of bag containers. Sample flow into each gas sampling bag is produced by controlled, partial evacuation of container void space surrounding the sample bags.

4.1.16 Critical Orifices. Glass or other suitable material, to fix the flow exiting the evacuable containers, and, in turn, to regulate the sample flow entering the sample bags. Sonic flow through each orifice should be approximately 0.050 L/min. Calibrate and place in-line between auxiliary sampling pump and bag.

4.1.17 Vacuum Tubing. To connect the rigid, evacuable bag containers to the auxiliary sampling pump.

4.1.18 Rate Meter. To be used in leak check procedures.

4.2 Gas Standards. Dilute gaseous butadiene in nitrogen at concentrations certified to $\pm$ 2%, commercially available from suppliers of high purity gases. Purchase cylinders containing nominal butadiene concentrations of 10, 100, and 1000 ppm, or at three other concentrations, to bracket the emission concentrations expected. Order the desired concentrations four or more weeks in advance of need to allow time for custom blending of gases by suppliers, when necessary.

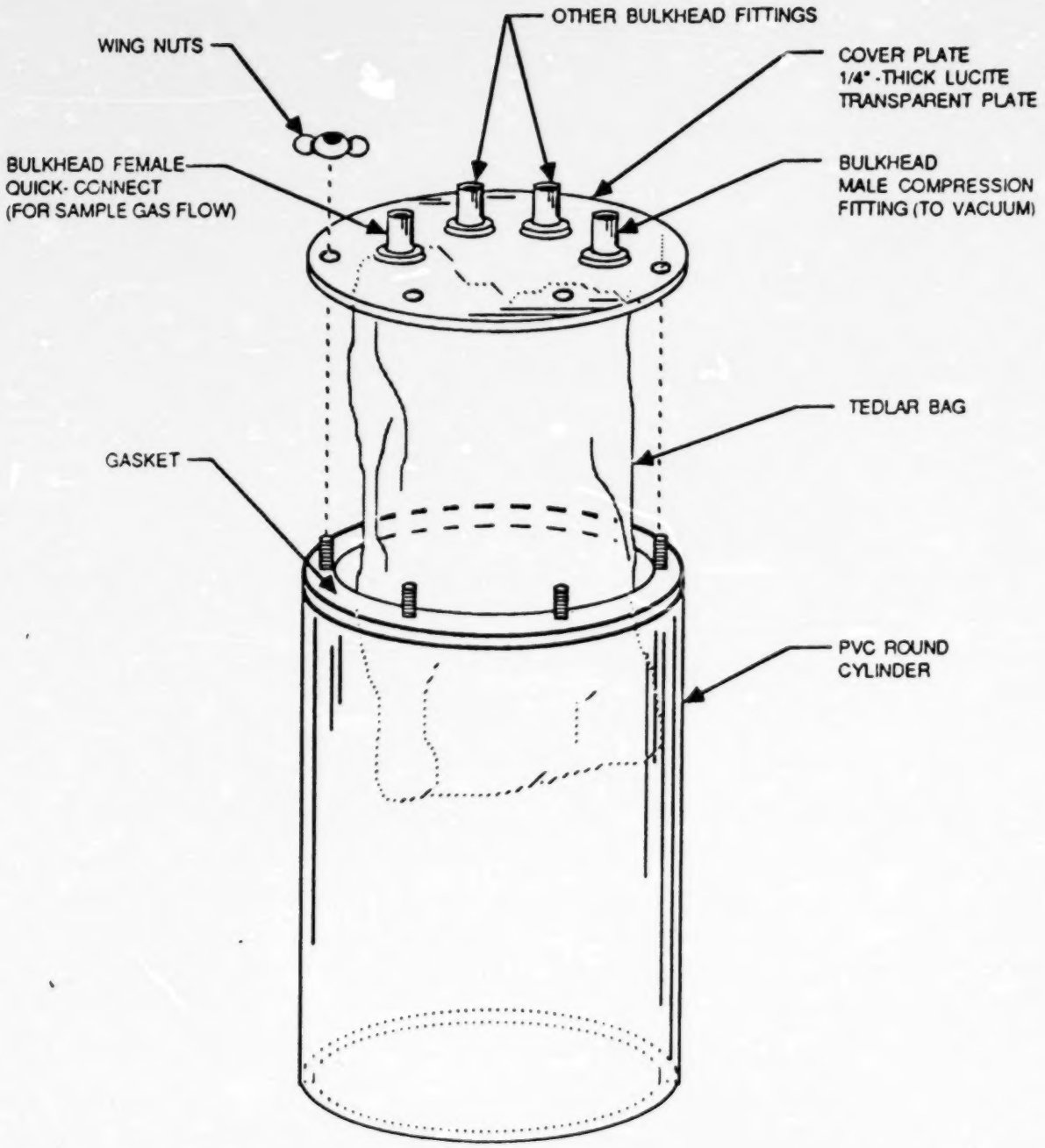

Figure A-2. PVC bag sampler.

4.3 Gas Chromatographic System. General criteria for the GC and peripheral hardware necessary for analysis of samples are outlined below.

4.3.1 Gas Chromatograph. Transportable, incorporating an FID, appropriate separation columns, a temperature-controlled gas sampling valve, and a column oven capable of maintaining stable temperatures of 30-100 °C.

4.3.2 Carrier Gas. Oxygen-/hydrocarbon-free nitrogen gas for optimum performance of separation columns and noiseless operation of detector. Minimum acceptable purity specifications recommended for carrier gas are dependent on specific column(s) and specific brand of detector used. Two carrier flows are required to create the backflush-to-vent configuration that is required for rapid sample analysis (refer to Figure A-3 and Sections 4.3.5 and 4.3.6).

4.3.3 Detector Feed Gases. High purity, hydrocarbon-free, compressed air and hydrogen for operation of FID. Minimum acceptable purity specifications recommended for detector feed gases are dependent on specific brand of detector used.

4.3.4 Recorder/Integrator. To record the output of the detector. If a strip chart recorder is used, provisions must be made for estimation of the recorded peak areas.

4.3.5 GC Columns. Two packed GC columns, serially combined in a backflush-to-vent configuration (refer to Figure 3 and Section 4.3.6). Resolution of closely related hydrocarbons from butadiene occurs on the rear column of the series, while high boiling sample components are backflushed and vented from the forward column. The first column separates butadiene and other permanent gases from the higher boiling sample components. One column adequate for this purpose is a 10' x 1/8" stainless steel column containing 20% SP-2100/0.1% Carbowax 1500 on 100/120 mesh Supelcoport. A 2 m x 1/8" stainless steel column containing 0.19% picric acid on 80/100 mesh Carbopack C, or other column similarly able to resolve C4 and unsaturated C4 hydrocarbons, is utilized for the final chromatographic separation.

4.3.6 Gas Sampling Valve. Stainless steel with ten ports and an inert gas sample loop. A schematic of the required backflush-to-vent sample valve configuration is included as Figure A-3. Maintain the entire valve/column assembly at a constant temperature in the GC column oven.

4.3.7 Gas Sample Loop. Stainless steel or Teflon. The sample loop's precise volume need not be known, but sample loop volumes of 0.1 to 1.0 mL are convenient for most analyses.

4.3.8 Gas Sample Loop Pump. To draw collected emissions samples from a gas sample bag through the sample loop at a nominal flow rate of 100 mL/min.

4.3.9 Rate Meter. To measure sample flow during loading of sample loop.

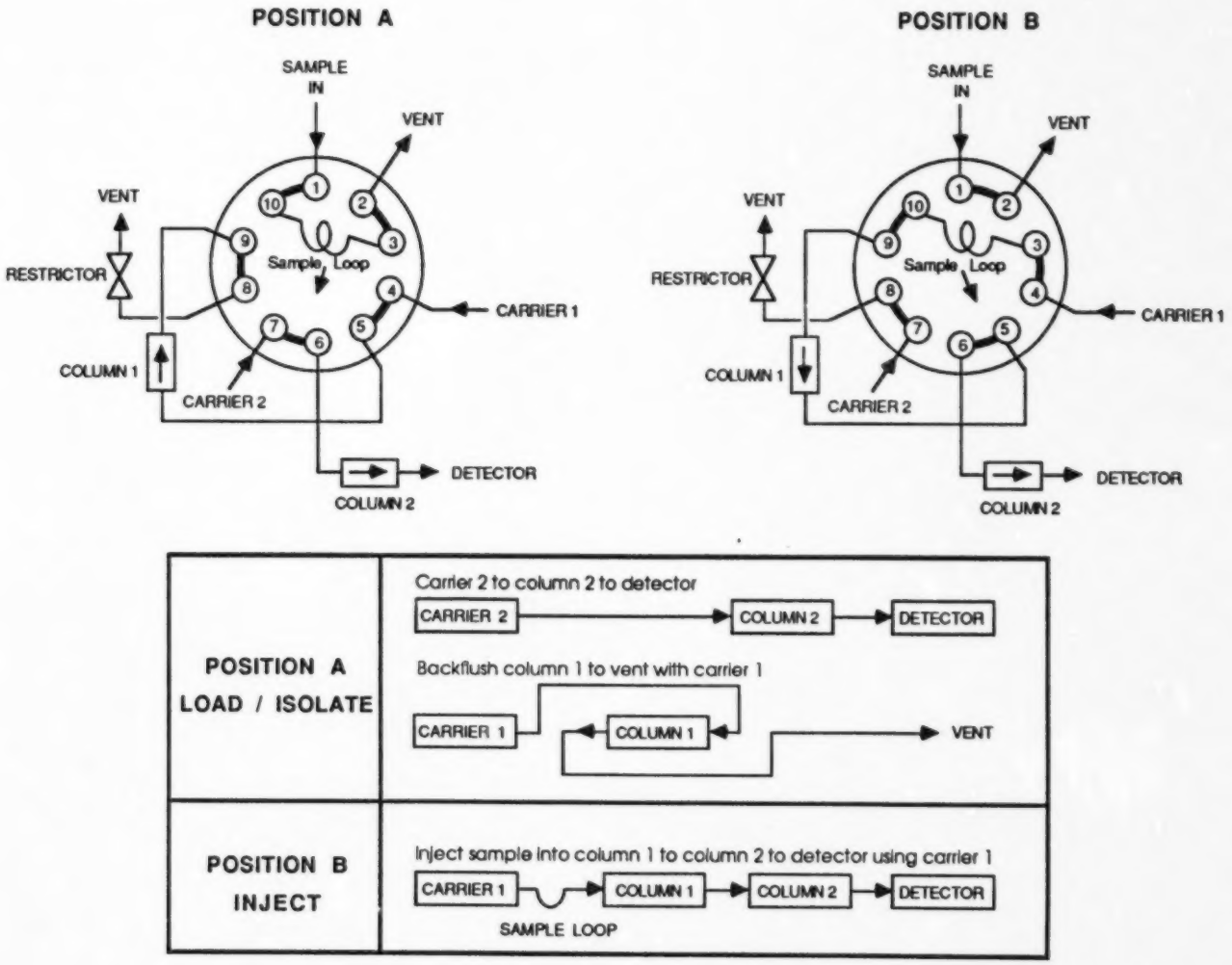

Figure A-3. Backflush-to-vent gas sample valve configuration.

5. Sampling Procedure

5.1 Pre-test Leak Checks. The Tedlar gas sampling bags and the rigid, evacuable containers are leak checked before traveling to the test site.

5.1.1 Leak Check of Tedlar Gas Sampling Bags. Leak check each Tedlar bag before sealing it in an evacuable container. A compression fitting incorporated during construction of each bag allows direct connection of the bag to the bulkhead female quick-connect fixed in the lid of individual evacuable containers. Screw the bags tightly to this quick-connect on the underside of the container lids and inflate bags to rigidity. Discard bags that show any loss of rigidity after standing overnight. Following leak check procedures, completely deflate the bags.

5.1.2 Leak Check of Rigid, Evacuable Containers. After ensuring that leakfree bags are attached to the lid of each evacuable container, liberally coat the rubber gaskets positioned atop the open container tops with silicone vacuum grease before screwing the lids tightly in place. To leak check individual evacuable containers, attach a water manometer to the bulkhead, male, compression fitting that is imbedded in each container lid. This fitting provides access to the container void space surrounding the enclosed sample bag, and allows the pressure changes within the container to be monitored. Seal other "open" fittings, create a positive pressure of 25 cm H_2O in the container by slowly filling the sample bag with a small volume of zero air via the female quick-connect connected to the enclosed bag. Any visible change in the level of the water in the manometer during a 30 second period indicates a leak. Isolate any leaks detected in the evacuable containers with a leak detection fluid.

5.2 Set-up of Sampling Apparatus. Attach the rear of the 3/8" OD Teflon probe line to the intake of primary sampling pump. Connect the outlet of the primary sampling pump to the sampling manifold. If a glass knockout chamber is used, mount it vertically and use Teflon tubing to connect the pump output to the inlet of the knockout chamber; attach the liquid drain line and associated flow control valve to the horizontal sidearm of the knockout; and connect the inlet of the stainless steel manifold, using Teflon tubing, to the outlet of the knockout chamber. Place the XAD-2 adsorption tube, if used, between the knockout and sampling manifold.

Use Teflon tubing to return excess sample gas to the emission conduit, or when the concentrations of process gases present create no explosion risk, pass excess sample gas through an activated charcoal filter before venting to the atmosphere at a safe distance from sampling personnel. Attach sample lines to the steel manifold.

Place the evacuable containers used to house the Tedlar bags in position for connection to the manifold sample lines using the quick-connects affixed in their lids. Do not connect the rigid, evacuable bag containers to the sampling manifold or to the auxiliary sampling pump until leak check procedures are completed.

5.3 On-site Leak Checks of Sampling Apparatus. The sampling apparatus is leak checked on-site in three sections.

5.3.1 Leak Check of Evacuation System. Plug the open ends of the vacuum tubing used to evacuate the bag containers. Connect the flow meter to the outlet of the auxiliary sampling pump, and start the pump. If the flow meter indicates any residual flow after a time sufficient to evacuate the vacuum lines, then a leak is present. Shut off the pump and unplug the vacuum lines when the leak check is complete.

5.3.2 Leak Check of Probe and Primary Sampling Pump. Remove the line leading from the outlet of the primary sampling pump to the sampling manifold, or to the glass knockout chamber when used, and attach the flow meter to the outlet of the pump. Plug the open end of the probe, and start the pump. If the flow meter indicates any residual flow after a time sufficient to evacuate the vacuum lines, then a leak is present. Shut off the pump, and unplug the probe when the leak check is complete.

5.3.3 Leak Check of Delivery System. Remove the flow meter from the outlet of the primary sampling pump, and reconnect the line leading to the sampling manifold, or to the glass knockout chamber when used. Visually inspect and tighten all connections. Position the probe to draw in ambient air, and start the pump. Adjust the flow exiting the sampling manifold, and/or the liquid drain line, if used, to maintain a positive pressure of 25 cm H_2O, as measured by the water manometer connected to the sampling manifold. A leak detection fluid may be used to isolate suspected leaks. Shut off the pump when the leak check is complete.

5.4 Final Assembly of Sampling Apparatus and Purge Procedure. Immediately prior to sampling, check the Tedlar gas sampling bags for residual gas, and evacuate as necessary. A large volume of in-drawn ambient air indicates that the bag may have leaked during transport. Attach the vacuum lines to the evacuable containers. Insert the probe into the emission conduit. Once the connection between the emission conduit and sampling apparatus is deemed leakfree, start the sample pump. Purge the delivery system for at least 5 minutes. During the purge, adjust the sample flow so that a positive pressure of approximately 10 cm H_2O, as measured by the water manometer attached to the sampling manifold, exists in the system.

5.5 Sample Collection. Following the purge of the delivery system, mate the quick-connects at the end of the manifold sample lines with the quick-connects joined to the gas sampling bags. Immediately start the auxiliary sampling pump to begin sampling. Adjust the sample flow at this point if the system pressure drops below approximately 4 cm H_2O, as measured by the water manometer. Rapid filling of an individual Tedlar bag indicates a leak in the surrounding container. Monitor the manifold pressure every 10 minutes as a drop in system pressure indicates a leak has formed in the delivery system. At the end of the 60 minute sampling period, switch off the auxiliary pump, and detach the manifold sample lines from the evacuable containers. Then, switch off the primary sampling pump.

6. GC Analysis

6.1 Column Configuration Used to Resolve Butadiene. Samples are rapidly and conveniently analyzed using an analytical system that includes two packed

GC columns connected in series and incorporated in a backflush-to-vent sample valve configuration (see Figure A-3). Such a system provides adequate separation of closely related hydrocarbons from butadiene on the second column in the series, while high boiling sample components are backflushed and vented from the forward column. The separation of butadiene and other permanent gases from the higher boiling sample components occurs on the first column; one column adequate for this purpose is a 10' x 1/8" stainless steel column containing 20% SP-2100/0.1% Carbowax 1500 on 100/120 mesh Supelcoport. A 2 m x 1/8" stainless steel column containing 0.19% picric acid on 80/100 mesh Carbopack C, or other column similarly able to resolve C4 and unsaturated C4 hydrocarbons, is utilized for the final chromatographic separation.

6.2 Instrument Operating Parameters.

6.2.1 Operating Parameters for Detector. For all analyses, fix the hydrogen and air flows to the FID at rates that give a stable flame. If the GC used includes internal metering orifices, supplying these gases at constant regulator pressures will accomplish this. Optimization of detector response according to the instructions provided by the manufacturer is recommended.

6.2.2 Temperatures of Heated Components. When using the columns listed in Section 6.1, set the oven to operate isothermally at 60°C. Maintain the detector temperature at 300°C.

6.2.3 Carrier Gas Flows. When using the columns listed in Section 6.1, set the forward flow through both columns at approximately 20 mL/min.

6.3 GC Equilibration. Prior to sample analysis, establish a stable baseline. Inject a nitrogen blank to distinguish any peaks arising from sample injection.

6.4 Introduction of Samples. Introduce cylinder standards directly into the sample loop at regulator pressures of approximately 140 kPa. Draw emission samples from the Tedlar bags and through the sample loop at nominal flow rates of 100 mL/min using a small pump. During sample loop loading of either standard cylinder gases or bag samples, purge the sample loop for a minimum of one minute. After cessation of standard or sample gas flow, allow the sample loop pressure to equilibrate to ambient pressure over a 10 second period before injecting loaded samples.

When using the recommended valve/column assembly, return the gas sample valve to its initial position approximately three minutes after injection of a gas sample. The resulting redirection of carrier flows isolates butadiene and other permanent gases, which have passed into the second column, from higher boiling sample components, which are backflushed from the first column to a vent. Butadiene and related C4 and C4 unsaturated hydrocarbons elute from the second column within about 12 minutes of the initial sample injection. The retention time of butadiene in Figure A-4, the example gas chromatogram, is 10.09 minutes.

6.5 Calibration Curve for Gas Chromatograph. Analyze the cylinder gas calibration standards as outlined in EPA Method 18. Use the peak areas resulting from analysis of these standards to establish a linear calibration

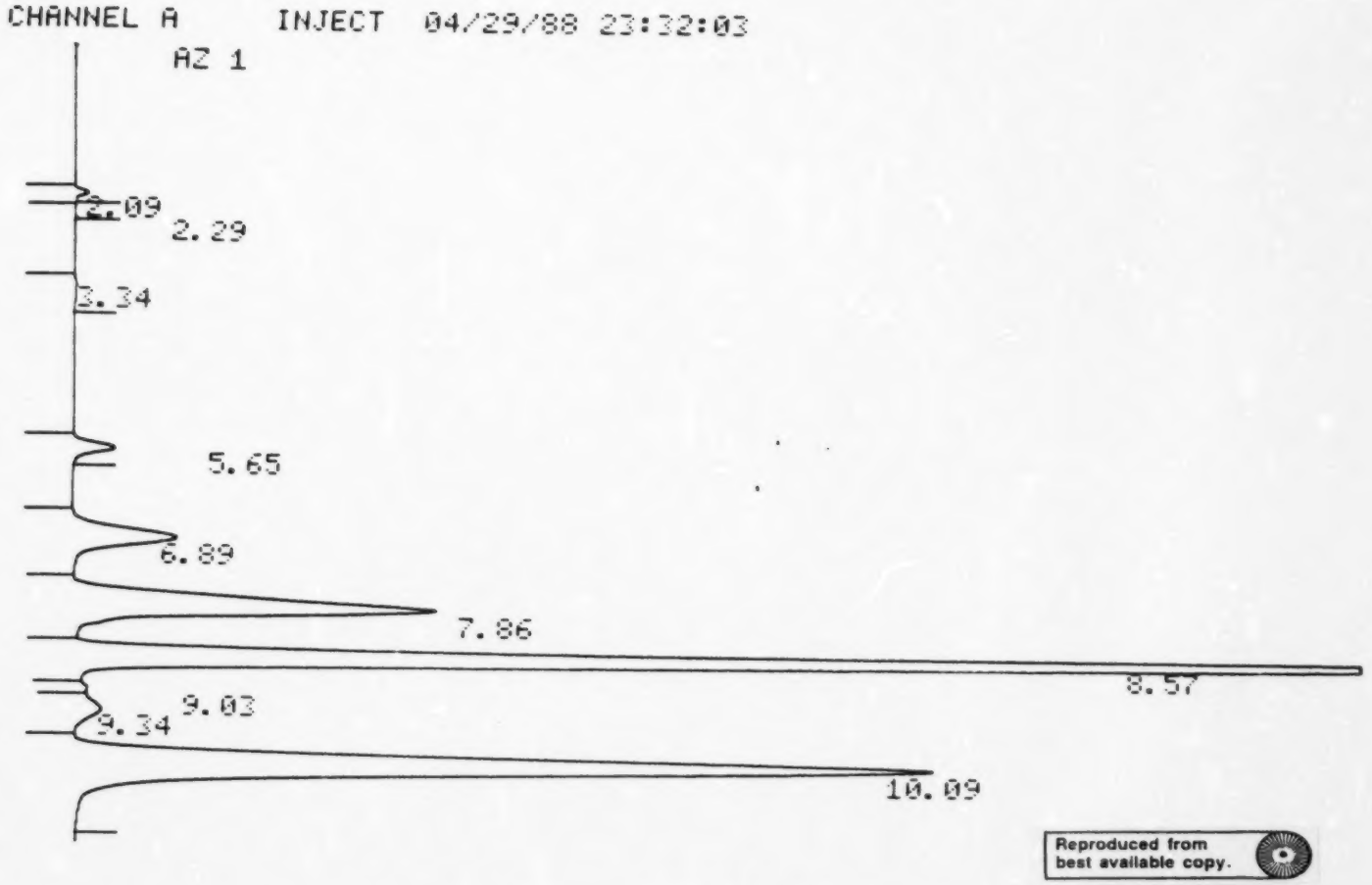

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Figure A-4. Example gas chromatogram.

curve relating detector response to the concentration of butadiene present in a sample.

6.6 Audit Analysis. Perform the analysis of audit samples, during calibration of the detector response, as set forth in EPA Method 18.

6.7 Calculation of Measured Butadiene Concentrations. Calculate the concentration of butadiene in the field samples using the detector response as set forth in EPA Method 18.

7. References

1. Federal Register, 51, No. 62, pp 11021-11022, April 1, 1986.

2. Method 18: Measurement of Gaseous Organic Compound Emissions by Gas Chromatography, 40 Code of Federal Regulations 60, July 1, 1987.

APPENDIX B

FIELD TEST DATA

SECOND BUTADIENE FIELD TEST - DAY 1

Job Name: Butadiene — Job Num. 4133
Analyst: JD Goodrich — Date: April 28, 1988

Butadiene Standard Calibration Curve by Linear Regression

Conc. (ppm)	Peak Area Run 1	Peak Area Run 2	Peak Area Average	Percent Deviation	Predicted Conc. (ppm)	Percent Deviation from Actual
10.1	253	249	251	0.7%	7.4	-26.8%
147.8	3887	3919	3903	0.4%	150.7	2.0%
1977	50532	50334	50433	0.2%	1977	0.0%

Standard Curve — Slope 25.48 — Intercept 62.83

Sample ID	Run 1 Area	Run 2 Area	Average	Percent Deviation	Butadiene Conc. (ppm)	Deviation from Mean
AUDIT	1383	1420	1401	1.3%	52.5	NA
51-A	8530	8465	8497	0.4%	331	9
51-B	8300	8255	8278	0.3%	322	1
51-C	8220	8187	8204	0.2%	320	-2
51-D	8068	8018	8043	0.3%	313	-8
	Average +/- 95% Confidence Interval				322 +/- 12	
	Standard Deviation		7.4			
	Coefficient of Variation			2.3%		
52-A	784	769	777	0.9%	28	4
52-B	468	458	463	1.1%	16	-8
52-C	728	726	727	0.1%	26	2
52-D	749	747	748	0.2%	27	3
	Average +/- 95% Confidence Interval				24 +/- 9	
	Standard Deviation		5.7			
	Coefficient of Variation			23.5%		

SECOND BUTADIENE FIELD TEST - DAY 1 (CONT.)

Butadiene Standard Calibration Curve by Linear Regression

Conc. (ppm)	Peak Area Run 1	Peak Area Run 2	Peak Area Average	Percent Deviation	Predicted Conc. (ppm)	Percent Deviation from Actual
10.1	253	249	251	0.7%	7.4	-26.8%
147.8	3887	3919	3903	0.4%	150.7	2.0%
1977	50532	50334	50433	0.2%	1977	0.0%
Standard Curve		Slope	25.48	Intercept	62.83	

Sample ID	Run 1 Area	Run 2 Area	Average	Percent Deviation	Butadiene Conc. (ppm)	Deviation from Mean
53-A	896	903	900	0.4%	33	3
53-B	863	863	863	0.0%	31	2
53-C	821	823	822	0.1%	30	0
53-D	690	673	682	1.2%	24	-5
	Average +/- 95% Confidence Interval				30 +/- 6	
	Standard Deviation		3.7			
	Coefficient of Variation			12.6%		
L54-A-R	11982	12229	12105	1.0%	473	45
L54-B-R	9772	9671	9721	0.5%	379	BAG LEAKED
L54-C-R	10066	9941	10003	0.6%	390	-38
L54-D-R	11847	12209	12028	1.5%	470	42
	Average +/- 95% Confidence Interval				444 +/- 117	
	Standard Deviation		47.0			
	Coefficient of Variation			10.6%		
54-A-R	12299	12198	12249	0.4%	478	19
54-B-R	12673	12288	12480	1.5%	487	29
54-C-R	10353	10214	10284	0.7%	401	-58
54-D-R	11830	12178	12004	1.4%	469	10
	Average +/- 95% Confidence Interval				459 +/- 62	
	Standard Deviation		39.2			
	Coefficient of Variation			8.5%		

SECOND BUTADIENE FIELD TEST - DAY 2

Job Name: Butadiene — Job Num. 4133
Analyst: JD Goodrich — Date: April 29, 1988

Butadiene Standard Calibration Curve by Linear Regression

Conc. (ppm)	Peak Area Run 1	Peak Area Run 2	Peak Area Average	Percent Deviation	Predicted Conc. (ppm)	Percent Deviation from Actual
10.1	306	303	305	0.5%	5.0	-50.7%
147.8	4335	4212	4273	1.4%	153.3	3.7%
1977	53052	53072	53062	0.0%	1977	0.0%

Standard Curve — Slope 26.76 — Intercept 171.21

Sample ID	Run 1 Area	Run 2 Area	Average	Percent Deviation	Butadiene Conc. (ppm)	Deviation from Mean
AUDIT	1562	1531	1546	1.0%	51.4	NA
55-A	3855	3799	3827	0.7%	148	-23
55-B	4571	4526	4548	0.5%	176	5
55-C	4590	4249	4420	3.9%	171	0
55-D	4906	4777	4841	1.3%	188	17
	Average +/- 95% Confidence Interval				171 +/- 27	
	Standard Deviation		16.7			
	Coefficient of Variation			9.8%		
56-A	12478	12417	12447	0.2%	486	-60
56-B	12249	12147	12198	0.4%	476	-70
56-C	19710	19366	19538	0.9%	764	218
56-D	12156	11276	11716	3.8%	457	-89
	Average +/- 95% Confidence Interval				546 +/- 233	
	Standard Deviation		146.0			
	Coefficient of Variation			26.7%		
61-A	13192	13233	13213	0.2%	487	61
61-B	12939	12892	12915	0.2%	476	50
61-C	11369	11380	11375	0.1%	419	-7
61-D	8744	8838	8791	0.5%	322	-104
	Average +/- 95% Confidence Interval				426 +/- 120	
	Standard Deviation		75.6			
	Coefficient of Variation			17.7%		

SECOND BUTADIENE FIELD TEST - DAY 2 (CONT.)

Job Name: Butadiene — Job Num. 4133
Analyst: JD Goodrich — Date: April 29, 1988

Butadiene Standard Calibration Curve by Linear Regression

Conc. (ppm)	Peak Area Run 1	Peak Area Run 2	Peak Area Average	Percent Deviation	Predicted Conc. (ppm)	Percent Deviation from Actual
10.1	306	303	305	0.5%	5.0	-50.7%
147.8	4335	4212	4273	1.4%	153.3	3.7%
1977	53052	53072	53062	0.0%	1977	0.0%

Standard Curve Slope 26.76 Intercept 171.21

Sample ID	Run 1 Area	Run 2 Area	Average	Percent Deviation	Butadiene Conc. (ppm)	Deviation from Mean
62-A	988	954	971	1.8%	30	1
62-B	839	805	822	2.0%	24	-4
62-C	1049	964	1007	4.2%	31	3
62-D	984	907	945	4.0%	29	0
Average +/- 95% Confidence Interval					29 +/- 5	
Standard Deviation			3.0			
Coefficient of Variation				10.5%		
63-A	2821	2782	2801	0.7%	98	-16
63-B	3348	3355	3351	0.1%	119	4
63-C	3331	3350	3340	0.3%	118	4
63-D	3443	3440	3441	0.0%	122	8
Average +/- 95% Confidence Interval					114 +/- 17	
Standard Deviation			10.9			
Coefficient of Variation				9.5%		

SECOND BUTADIENE FIELD TEST - DAY 3

Job Name: Butadiene — Job Num. 4133
Analyst: JD Goodrich — Date: April 30, 1988

Butadiene Standard Calibration Curve by Linear Regression

Conc. (ppm)	Peak Area Run 1	Peak Area Run 2	Peak Area Average	Percent Deviation	Predicted Conc. (ppm)	Percent Deviation from Actual
10.1	333	330	332	0.5%	8.7	-13.8%
147.8	4123	4332	4227	2.5%	149.3	1.0%
1977	54504	55232	54868	0.7%	1977	0.0%

Standard Curve — Slope 27.71 — Intercept 90.53

Sample ID	Run 1 Area	Run 2 Area	Average	Percent Deviation	Butadiene Conc. (ppm)	Deviation from Mean
AUDIT	1481	1477	1479	0.1%	50.1	NA
71-A	3873	4027	3950	1.9%	139	-10
71-B	4274	4281	4278	0.1%	151	2
71-C	4298	4268	4283	0.4%	151	2
71-D	4309	4425	4367	1.3%	154	5
	Average +/- 95% Confidence Interval				149 +/- 11	
	Standard Deviation		6.6			
	Coefficient of Variation			4.5%		
L72-A	451	457	454	0.7%	13.1	-0.7
L72-B	484	490	487	0.6%	14.3	0.5
L72-C	486	494	490	0.9%	14.4	0.6
L72-D	464	468	466	0.5%	13.5	-0.3
	Average +/- 95% Confidence Interval				13.8 +/- 1.0	
	Standard Deviation		0.6			
	Coefficient of Variation			4.5%		
72-A	432	439	436	0.9%	12.5	-0.4
72-B	448	458	453	1.2%	13.1	0.2
72-C	455	463	459	0.9%	13.3	0.4
72-D	436	440	438	0.5%	12.6	-0.3
	Average +/- 95% Confidence Interval				12.8 +/- 0.6	
	Standard Deviation		0.4			
	Coefficient of Variation			3.2%		

SECOND BUTADIENE FIELD TEST - DAY 3 (CONT.)

Butadiene Standard Calibration Curve by Linear Regression

Conc. (ppm)	Peak Area Run 1	Peak Area Run 2	Peak Area Average	Percent Deviation	Predicted Conc. (ppm)	Percent Deviation from Actual
10.1	333	330	332	0.5%	8.7	-13.8%
147.8	4123	4332	4227	2.5%	149.3	1.0%
1977	54504	55232	54868	0.7%	1977	0.0%

Standard Curve Slope 27.71 Intercept 90.53

Sample ID	Run 1 Area	Run 2 Area	Average	Percent Deviation	Butadiene Conc. (ppm)	Deviation from Mean
73-A	95659	97390	96525	0.9%	3480	2
73-B	94872	95050	94961	0.1%	3424	-54
73-C	96905	98760	97832	0.9%	3527	49
73-D	96246	96823	96535	0.3%	3481	3
	Average +/- 95% Confidence Interval				3478 +/- 68	
	Standard Deviation		42.4			
	Coefficient of Variation			1.2%		

SECOND BUTADIENE FIELD TEST - POST TEST (DAY 8)

Job Name: Butadiene Job Num. 4133
Analyst: JD Goodrich Date: May 5, 1988

Butadiene Standard Calibration Curve by Linear Regression

Conc. (ppm)	Peak Area Run 1	Peak Area Run 2	Peak Area Average	Percent Deviation	Predicted Conc. (ppm)	Percent Deviation from Actual
10.1	389	383	386	0.8%	7.2	-29.1%
147.8	3145	3193	3169	0.8%	151.0	2.1%
1977	38684	38347	38515	0.4%	1977	0.0%

Standard Curve Slope 19.36 Intercept 246.98

Sample ID	Run 1 Area	Run 2 Area	Average	Percent Deviation	Butadiene Conc. (ppm)		Deviation from Mean
AUDIT	1154	1141	1148	0.5%	46.5		NA
73-A	63828	64305	64067	0.4%	3297	3480	-5.3%
73-C	53483	53913	53698	0.4%	2761	3527	-21.7%
73-D	52247	52727	52487	0.5%	2698	3481	-22.5%
56-A	8437	8488	8463	0.3%	424	486	-12.7%
54-C	7692	7738	7715	0.3%	386	401	-3.8%
51-A	6750	6768	6759	0.1%	336	331	1.6%
55-D	3423	3396	3410	0.4%	163	188	-13.1%

SECOND BUTADIENE FIELD TEST - POST-TEST (DAY 9)

Job Name: Butadiene Job Num. 4133
Analyst: JD Goodrich Date: May 6, 1988

Butadiene Standard Calibration Curve by Linear Regression

Conc. (ppm)	Peak Area Run 1	Peak Area Run 2	Peak Area Average	Percent Deviation	Predicted Conc. (ppm)	Percent Deviation from Actual
10.1	240	226	233	3.0%	9.6	-5.4%
147.8	3143	3131	3137	0.2%	148.4	0.4%
1977	41274	41494	41384	0.3%	1977	0.0%

Standard Curve Slope 20.92 Intercept 33.43

Sample ID	Run 1 Area	Run 2 Area	Average	Percent Deviation	Butadiene Conc. (ppm)		Deviation from Mean
AUDIT	1093	1092	1092	0.0%	50.6		NA
71-D	3024	3047	3035	0.4%	144	154	-6.8%
63-D	1849	1863	1856	0.4%	87	112	-22.2%
53-A	810	810	810	0.0%	37	33	12.5%
52-A	579	578	578	0.1%	26	28	-6.9%
72-A	336	336	336	0.1%	14.5	12.5	15.7%
72-B	337	338	337	0.0%	14.5	13.1	11.0%
72-C	320	320	320	0.0%	13.7	13.3	2.9%
72-D	329	330	330	0.1%	14.2	12.6	12.5%
L72-A	369	378	373	1.2%	16.3	13.1	24.1%
L72-B	498	501	499	0.3%	22.3	14.3	55.8%
L72-C	454	455	454	0.1%	20.1	14.4	39.8%
L72-D	386	392	389	0.7%	17.0	13.5	25.9%
73-A	67264	69034	68149	1.3%	3257	3480	-6.4%